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IS 13963-2 (1994): Chemical analysis of cadmium metal, Part 2: Determination of nickel, arsenic, antimony and thallium by spectrometric methods [MTD 9: Lead, Zinc, Cadmium, Tin, Antimony and their Alloys]

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Indian Standard

CHEMICAL ANALYSIS OF CADMIUM METAL

PART 2 DETERMINATION OF NICKEL, ARSENIC, ANTIMONY AND THALLIUM BY SPECTROPHOTOMETRIC METHODS

UDC 669·73 : 543·42 [546·74]

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NEW DELHI 110002

February 1994 **Price Group 3**

Methods of Chemical Analysis of Non-Ferrous Metals Sectional Committee, MTD 28

FOREWORD

This Indian Standard was adopted by the Bureau of Indian Standards, after the draft finalized by the Methods of Chemical Analysis of Non-Ferrous Metals Sectional Committee had been approved by the Metallurgical Engineering Division Council.

IS 6344 : 1985 'Specification for cadmium metals' covers the requirements of various grades of this material. The Sectional Committee responsible for preparation of this standard decided that the methods of chemical analysis of various constituents prescribed in IS 6344 : 1985 may be covered in different parts of the standard. Accordingly this standard (Part 2) has been prepared to describe the chemical analysis of cadmium metal for nickel, arsenic, antimony and thallium content by spectrophotometric methods.

The Part 1 of this standard describes the atomic absorption spectrometric methods for determination of copper, zinc, lead and iron as referee methods. It also describes spectrophotometric method for determination of copper and iron and polarographic method for determination of zinc and lead in cadmium metal as alternate methods.

In reporting the results of a test or analysis made in accordance with this standard, if the final value, observed or calculated, is to be rounded off, it shall be done in accordance with IS 2 : 1960 'Rules for rounding off numerical values (*revised*)'.

Indian Standard

CHEMICAL ANALYSIS OF CADMIUM METAL

PART 2 DETERMINATION OF NICKEL, ARSENIC, ANTIMONY AND THALLIUM BY SPECTROPHOTOMETRIC METHODS

1 SCOPE

This standard (Part 2) describes spectrophotometric methods for determination of nickel, arsenic, antimony and thallium in the ranges given below:

Element	*Concentration* (Percent by mass, *Max*)
Nickel	0·003
Arsenic	0·003
Antimony	0·001
Thallium	0·003

2 REFERENCES

The following Indian Standards are necessary adjuncts to this standard:

IS No.	*Title*
264 : 1976	Nitric acid (*second revision*)
265 : 1993	Hydrochloric acid (*fourth revision*)
266 : 1993	Sulphuric acid (*third revision*)
1070 : 1992	Reagent grade, water (*third revision*)
1817 : 1961	Methods of sampling of non-ferrous metals for chemical analysis

3 SAMPLING

Sample shall be drawn and prepared in accordance with the procedure laid down in IS 1817 : 1961 and IS 6344 : 1985.

4 QUALITY OF REAGENTS

Unless specified otherwise, analytical grade reagents and distilled water (*see* IS 1070 : 1992) shall be employed for the test.

5 DETERMINATION OF NICKEL

5.1 Outline of the Method

Nickel from the sample solution is extracted as its dimethylglyoxime complex in chloroform. From the chloroform extract it is further extracted and brought to hydrochloric acid medium and estimated spectrophotometrically as nickel dimethylglyoxime complex at 445 nm.

5.2 Reagents

5.2.1 *Hydrochloric Acid*, rd = 1·16 (Conforming to IS 265 : 1987).

5.2.2 *Dilute Nitric Acid*, 1 : 1 (*v/v*)

5.2.3 *Citric Acid Solution*, 20 percent (*m/v*)

5.2.4 *Hydroxylamine Hydrochloride Solution*, 10 percent (*m/v*)

5.2.5 *Ammonium Hydroxide*, pure

5.2.6 *Ammonium Hydroxide Solution*, 2 percent (*v/v*)

5.2.7 *Dimethylglyoxime Solution* (1 percent)

Dissolve 1 g of dimethylglyoxime in 100 ml of ethyl alcohol.

5.2.8 *Bromine Water*, saturated

5.2.9 *Dilute Hydrochloric Acid* (0·5 *N*)

Dilute 39·3 ml of hydrochloric acid to 1 litre with water.

5.2.10 *Chloroform*

5.2.11 *Standard Nickel Solution* (1 ml = 100 µg Ni)

Dissolve 0·025 g of pure nickel in minimum quantity of dilute nitric acid (0·5 *N*). Boil off oxides of nitrogen. Cool and make up to 250 ml.

5.2.11.1 *Standard nickel solution* (1 ml = 1 µg Ni)

Dilute 1 ml of standard solution (**5.2.11**) to 100 ml with distilled water.

5.2.12 *Cadmium Solution* (1 ml = 100 mg Cd)

Transfer 10 g of cadmium metal (purity 99·9 percent, *Min*) to a 150 ml beaker. Add 5 ml of water and then add 20 ml nitric acid in small increments. When dissolution is complete boil gently to remove oxides of nitrogen and cool. Dilute to 100 ml in volumetric flask and mix.

5.3 Procedure

5.3.1 Weigh 10 g of sample and transfer to a beaker. Add 35 ml of hydrochloric acid and

10 ml of dilute nitric acid (**5.2.2**). When dissolution is complete boil to syrupy consistency. Transfer the contents to 100 ml volumetric flask, make up to mark and mix thoroughly.

5.3.2 Transfer 10 to 25 ml aliquot (**5.3.1**) (containing 5 to 15 μg of nickel) to a 125 ml separating funnel. Add 5 ml of citric acid solution followed by 1 ml of hydroxylamine hydrochloride solution (**5.2.4**). Swirl to mix after each addition. Neutralize the solution to litmus with ammonia and then add 3 ml of dimethylglyoxime reagent. Mix and let stand for a few minutes.

5.3.3 Add 10 ml of chloroform. Shake for one minute. Allow layers to separate. Collect the chloroform layer in another 125 ml separating funnel. Repeat the extraction twice more with 10 ml portion of chloroform. Discard the aqueous layer.

5.3.4 Wash the combined extracts with 10 ml of ammonia (2 percent). Repeat the washing to ensure the removal of copper, etc. Shake the combined ammonia washings with a few ml of chloroform and add this to the main chloroform extract discarding washings.

5.3.5 Shake the chloroform extract with three 5 ml portions of hydrochloric acid (0·5 *N*) and collect the acid extract in a 25 ml graduated cylinder. Add bromine water drop by drop till the acid extract shows a distinct yellow colour. Now add strong ammonia solution again, drop by drop till bromine colour is discharged and then add one ml in excess. Cool the cylinder and contents, if necessary, and then add 1 ml of dimethylglyoxime reagent and make up to 25 ml with water. Determine the absorbance of the solution at 445 nm. A blank is used as a reference solution.

5.3.6 *Calibration Curve*

Transfer 0, 1, 2, 5, 10 and 15 ml of standard nickel solution (**5.2.11.1**) into six 125 ml separating funnels. Add an appropriate quantity of the cadmium solution (**5.2.12**) to each separating funnel equal to the concentration of cadmium in the corresponding test solution. Follow rest of the procedure as specified in **5.3.2** to **5.3.5**. Measure the absorbance of each solution at 445 nm and construct the calibration curve.

5.3.7 *Calculation*

$$\text{Nickel, percent by mass} = \frac{m \times 100}{M \times 10^6}$$

where

m = mass in μg, of nickel in the sample as read from calibration curve; and

M = mass in g, of sample taken.

6 DETERMINATION OF ARSENIC

6.1 Outline of the Method

Arsenic is separated as arsenic trichloride from interfering elements like antimony by distillation. Arsene evolved is absorbed in silver diethyldithiocarbamate in pyridine and then estimated spectrophotometrically at 56° nm.

6.2 Reagents

6.2.1 *Nitric Acid*, rd = 1·42 (conforming to IS 265 : 1993)

6.2.2 *Sulphuric Acid*, rd = 1·84 (conforming to IS 266 : 1977)

6.2.3 *Sulphurous Acid*, pure

6.2.4 *Phosphoric Acid*, rd = 1·75

6.2.5 *Hydrochloric Acid*, rd = 1·16 (conforming to IS 264 : 1993)

6.2.6 *Potassium Iodide Solution*, 15 percent (*m/v*)

6.2.7 *Stannous Chloride Solution*

Dissolve 40 g stannous chloride dihydrate in 100 ml hydrochloric acid.

6.2.8 *Lead Acetate Solution*

Dissolve 10 g lead acetate in 100 ml water. Soak the glass wool in the scrubber with this solution, drain and dry before the evolution of the arsene.

6.2.9 *Silver Diethyldithiocarbamate Reagent*

A cooled solution of silver nitrate (1·7 g in 100 ml water) is added to a cooled solution of sodium diethyl dithiocarbamate (2·25 g in 100 ml water). The lemon yellow precipitate is filtered off, washed thoroughly with distilled water and dried in a vacuum desiccator below 20°C (Note 1).

NOTE 1 — This reagent must be prepared below 20°C to prevent its decomposition.

6.2.10 *Pyridine*

Elute reagent grade pyridine through an alumina column, 25 mm in diameter and 150 mm in height at the rate of approximately 150 ml per hour to remove coloured material.

6.2.11 *Arsene Absorbing Solution*

Dissolve one gram of silver diethyldithiocarbamate in 200 ml of pyridine (**6.2.10**) and filter.

6.2.12 *Zinc Metal,* fine granulated.

6.2.13 *Standard Arsenic Solution* (1 ml = 100 µg As)

Dissolve 0·132 g of arsenic trioxide in 2 ml of (1 *N*) sodium hydroxide. Dilute with water. Make slightly acidic with hydrochloric acid. Dilute to one litre with water.

6.2.13.1 *Standard arsenic solution* (1 ml = 1 µg As)

Dilute 10 ml of standard solution (**6.2.13**) to 100 ml with water and mix.

6.3 Apparatus

6.3.1 *Distillation Apparatus, see* Fig. 1 for typical apparatus.

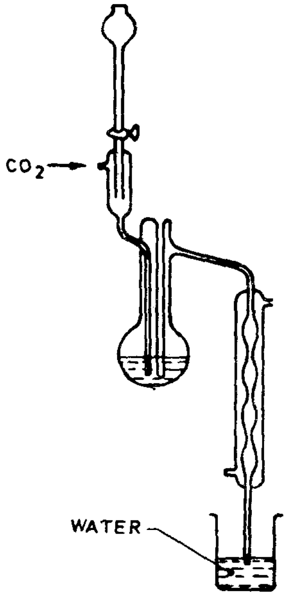

FIG. 1 DISTILLATION APPARATUS

6.3.2 *Liberation and Absorption Apparatus, see* Fig. 2

6.4 Procedure

6.4.1 Evaporate a suitable aliquot (25 to 50 ml) of sample as prepared in **5.3.1** to dryness on a water bath (Note 2). Add 15 ml of dilute sulphuric acid and evaporate it to 5 ml. Add 30 to 40 ml of sulphurous acid and evaporate to 10 ml.

NOTE 2 — To prevent any possible loss of arsenic, antimony and their chloride salts during evaporation, it is desirable to prepare sample in mixture of nitric acid and sulphuric acid.

6.4.2 Transfer the solution to the distillation flask of distillation apparatus (*see* Fig. 1) with 40 ml hydrochloric acid. The tip of the condenser dips into 25 ml of water contained in conical flask or a beaker. Distil off arsenic at 111° to 112°C until the residual volume is 20 ml. Add 10 ml more of hydrochloric acid and continue distillation till the volume is again reduced to 20 ml. The receiver contains arsenic.

6.4.3 Change the receiver and distil antimony chloride in a current of carbon dioxide after adding 5 ml of phosphoric acid. Continue distillation till about 20 ml of distillate is collected at the rate of 20 to 30 drops per minute. During distillation, keep adding hydrochloric acid to the distilling flask to keep the volume constant. The temperature of distillation shall be 155° to 165°C. Preserve this distillate for the estimation of antimony.

6.4.4 Transfer the distillate of arsenic collected under **6.4.2** to a 250 ml conical flask for liberation of arsene (Fig. 2). Dilute to 100 ml with water. Add 5 ml of hydrochloric acid, 2 ml of potassium iodide (15 percent) and 1 ml of stannous chloride solution. Swirl the flask and allow to stand for 15 minutes to ensure reduction of all arsenic to trivalent form.

6.4.5 Place 3 ml of arsene absorbing solution (**6.2.11**) in the absorbing tube which is connected to the scrubber packed with glass wool impregnated with lead acetate solution.

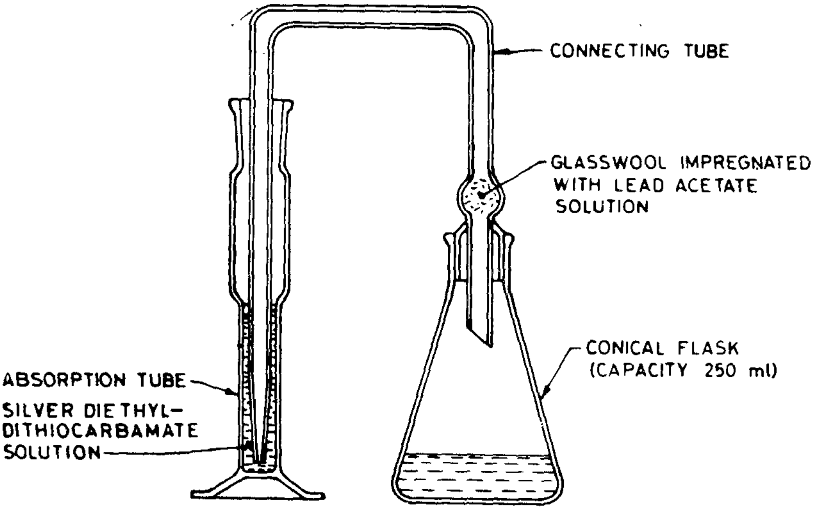
CONNECTING TUBE
GLASSWOOL IMPREGNATED WITH LEAD ACETATE SOLUTION
CONICAL FLASK (CAPACITY 250 ml)
ABSORPTION TUBE
SILVER DIETHYL-DITHIOCARBAMATE SOLUTION

FIG. 2 TYPICAL APPARATUS FOR THE LIBERATION AND ABSORPTION OF ARSENE

6.4.6 Add 3 g of zinc granules to the conical flask containing reduced arsenic (**6.4.4**). Immediately close the flask with the scrubber assembly. Allow to stand for about 30 minutes for the reaction to complete. The arsene is absorbed in the silver diethyldithiocarbamate solution (**6.2.11**) producing purplish red colour.

6.4.7 Transfer the solution (**6.4.6**) to the cell of optical length 1 cm. Measure the absorbance of the solution at 560 nm using spectrophotometer.

6.4.8 *Calibration Curve*

Pipette 0, 1, 2, 3, 5, 7 and 10 ml of the standard arsenic solution (**6.2.13.1**) into each of seven 250 ml flasks. Add 15 ml of hydrochloric acid, dilute to 100 ml and add 2 ml potassium iodide (15 percent) and 1·0 ml stannous chloride. Swirl the flask and proceed as in **6.4.5** and **6.4.6**. Measure absorbance in each case and draw the calibration curve.

6.4.9 *Calculation*

$$\text{Arsenic, percent by mass} = \frac{m \times 100}{M \times 10^6}$$

where

m = mass in μg, of arsenic in the sample as read from calibration curve; and

M = mass in g, of the arsenic sample.

7 DETERMINATION OF ANTIMONY

7.1 Outline of the Method

Antimony is separated from interfering elements by distillation. From the distillate, pentavalent antimony is extracted by isopropyl ether and estimated as its rhodamine B complex at 540 nm.

7.2 Reagents

7.2.1 *Hydrochloric Acid*, rd = 1·25 (conforming to IS 265 : 1993)

7.2.2 *Hydrochloric Acid*, 1 M and 3 M

7.2.3 *Sulphuric Acid*, rd = 1·84 (conforming to IS 266 : 1993)

7.2.4 *Sulphurous Acid*

7.2.5 *Phosphoric Acid*

7.2.6 *Ceric Sulphate Solution* (0·1 *N*)

Dissolve 3·3 g of ceric sulphate in 100 ml of sulphuric acid (0·5 *N*).

7.2.7 *Hydroxylamine Hydrochloride Solution* (0·1 percent), in hydrochloric acid (1 M).

7.2.8 *Isopropyl Ether*

Shake 150 ml isopropyl ether with 50 ml of hydrochloric acid (3 M). Drain off aqueous layer.

7.2.9 *Rhodamine B Reagent*

Dissolve 0·02 g of the reagent in 100 ml of hydrochloric acid (1 M).

7.2.10 *Standard Antimony Solution* (1 ml = 100 μg Sb)

Dissolve 0·025 g of pure antimony in 10 ml of sulphuric acid. Heat to fumes. Dilute with 10 ml of water. Add 5 ml of tartaric acid (10 percent) and dilute to 250 ml with water.

7.2.10.1 *Standard antimony solution* (1 ml = 1 μg Sb)

Transfer 1 ml of standard solution (**7.2.10**) to 100 ml volumetric flask, dilute to volume with water and mix.

7.3 Procedure

7.3.1 Transfer the distillate of antimony preserved in **6.4.3** to 150 ml separating funnel with 20 ml of water. Mix well.

Add a little ceric sulphate solution and mix again. Blow air into the funnel to expel any chlorine gas that might have been formed. Now reduce the excess ceric ions with a little hydroxylamine hydrochloride (1 percent). Add 10 ml of water and mix.

NOTE 3 — Sample at this stage shall be about 6 *N* with respect of hydrochloric acid.

7.3.2 Add 10 ml of isopropyl ether and shake for one minute. Allow layers to separate. Discard the aqueous layer. Shake the ether extract with 5 ml of rhodamine B solution. Measure the absorbance of the ether layer in a spectrophotometer at 540 nm. A blank taken simultaneously with the sample is used as reference solution.

7.3.3 *Calibration Curve*

Transfer 0, 1, 2, 3, 4 and 5 ml of standard antimony solution (**7.2.10.1**) into each of six 125 ml separating funnels. Dilute to 20 ml. Add 20 ml of hydrochloric acid. Mix well and add a little ceric sulphate solution and continue to proceed as **7.3.1** and **7.3.2**. Obtain absorbance in each case and draw the calibration curve.

7.3.4 *Calculation*

$$\text{Antimony, percent by mass} = \frac{m \times 100}{M \times 10^6}$$

where

m = mass in μg, of the antimony present in the sample and read from the calibration curve, and

M = mass in g, of the sample taken.

8 DETERMINATION OF THALLIUM

8.1 Outline of the Method

Sample is dissolved in hydrobromic acid-bromine mixture from which thallium is extracted with isopropyl ether. The ether extract of thallium is complexed with rhodamine B and estimated spectrophotometrically at 540 nm.

8.2 Reagents

8.2.1 *Hydrobromic Acid — Bromine Mixture*

Add 25 ml of bromine to 225 ml of hydrobromic acid (48 percent) and mix well.

8.2.2 *Rhodamine B Reagent*

Dissolve 0·10 g of rhodamine B in 500 ml of hydrochloric acid (1·0 *N*).

8.2.3 *Isopropyl Ether*

8.2.4 *Standard Thallium Solution* (1 ml = 100 μg Tl)

Dissolve 0·10 g of pure thallium metal in 10 ml of dilute nitric acid (1 : 1). After completion of reaction add 10 ml of dilute sulphuric acid (1 : 1) and heat to fumes. Cool, dissolve in water, cool again and finally make up to 1 000 ml.

8.2.4.1 *Standard thallium solution* (1 ml = 2 μg Tl)

Dilute 2 ml of standard solution (**8.2.4**) to 100 ml with water and mix.

8.2.5 *Water*, preferably double distilled.

8.3 Procedure

8.3.1 Weigh accurately 0·5 to 1·0 g sample sawings or drillings containing 0·1 to 10 μg of Tl into a dry 150 ml beaker. Add 5·0 ml of the hydrobromic acid-bromine mixture and immediately cover the beaker with a watch glass. When the reaction has slowed down, warm on a low temperature to effect complete dissolution of the sample. Rinse down the cover glass and sides of the beaker with 5 ml of water, mix and then heat the solution just below its boiling point until the excess of bromine is expelled.

8.3.2 Cool to room temperature, then transfer the solution to 60 ml separating funnel, rinsing out the beaker with distilled water (**8.2.5**). Make up the volume to 25 ml and mix well. Add 10 ml of isopropyl ether and shake for 1 minute. Allow layers to separate. Carefully drain the aqueous layer. Add 5 ml of rhodamine B solution and shake for 90 seconds. Allow phases to separate again. Drain off the aqueous layer. Measure the absorbance of the ether extract at 540 nm on a spectrophotometer. A reagent blank carried through all the stages of the procedure is used as a reference solution for absorbance measurement.

NOTE 4 — The ether extract may be centrifuged if it is not sufficiently clear before absorbance measurement.

8.3.3 *Calibration Curve*

To each of the six 150 ml beakers transfer 0, 1, 2, 3, 4 and 5 ml of standard thallium solution (**8.2.4.1**). Add 5 ml of the hydrobromic acid-bromine mixture (*see* Note 5). Cover the beakers with watch glasses and proceed as in **8.3.1** and **8.3.2**. Draw the calibration curve with microgram of thallium against absorbance.

NOTE 5 — The standard solution should preferably contain, an equivalent amount of pure cadmium metal as do the sample.

8.3.4 *Calculation*

$$\text{Thallium, percent by mass} = \frac{m \times 100}{M \times 10^6}$$

where

m = mass in μg, of thallium found from the calibration curve; and

M = mass in mg, of sample taken.

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This Indian Standard has been developed from Doc: No. MTD 28 (3492)

Amendments Issued Since Publication

Amend No.	Date of Issue	Text Affected

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Printed at Paragon Enterprises, Delhi, India